

METHOD FOR CHEMICAL VAPOR
DEPOSITION OF SILICON ON TO SUBSTRATES FOR
USE IN CORROSIVE AND VACUUM ENVIRONMENTS

5 CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of, and
claims priority from, U.S. Application Serial No.
10/382,040, filed on March 5, 2003.

10 BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method for vapor
deposition of silicon on substrates to impart properties
15 for use in corrosive and vacuum environments. More
particularly, the present invention relates to an
improved method of applying a silicon passivation layer
to the surfaces of substrates.

2. Brief Description of the Related Art

20 The present invention overcomes many known
deficiencies by using silicon as a passivation layer for
a variety of substrates, including those comprised of
metal (ferrous and non-ferrous), glass, carbon, copper,
quartz, nickel-containing ferrous alloys, titanium,
25 aluminum and ceramics. Substrates comprised of these
materials generally have been known to have undesirable
properties, which may, for example include one or more of
the following: chemisorption of other molecules;
reversible and irreversible physisorption of other
30 molecules; catalytic activity with other molecules;

5 allowing of attack from foreign species, resulting in a
molecular, structural and/or cosmetic breakdown of the
substrate surfaces and/or bulk; offgassing or outgassing
of volatile materials (e.g. water vapor and organics),
diffusion or permeation or other processes resulting in
10 the release of gas molecules from a substrate into a
vacuum environment resulting in extensive time required
to reach a target vacuum and/or the inability to achieve
a target vacuum and/or the inability to maintain a target
vacuum; hydrogen permeation of a substrate where the
15 inner portion is subjected to vacuum.

Previous art has focused on layers of silicon
modified by oxidation to prevent adsorption. Other
previous art has looked at the use of silanes or silicon
hydrides passed over metal surfaces at low temperatures
20 to passivate the metal surface.

This invention has utility for substrates which may
come in contact with species which degrade, are adsorbed
or attack metal surfaces (such as organo-sulfurs,
hydrogen sulfide, alcohols, acetates, metal hydrides,
25 hydrochloric acid, nitric acid, sulfuric acid).

The prior art has utilized a single treatment of
silicon hydride gases, either for silicon deposition or
adsorption to metal surfaces, to impart passivation.
This invention utilizes singular and multiple treatments
30 with the silicon hydride gases to impart desired
passivation by deposition of silicon.

5 Prior art also indicates preparation of metals surfaces by exposure to reducing gases prior to silicon deposition. This invention does not utilize such a pretreatment to achieve a passive surface.

U.S. Patent 4,579,752 issued on April 1, 1986 to
10 Lawrence A. Dubois, et al. for an "Enhanced Corrosion Resistance of Metal Surfaces" discloses a method to increase the anti-corrosive characteristics of metal surfaces by creating a protective surface coating with silane gas in the presence of an oxidizing agent to
15 produce a protective layer of SiO and excludes the use of iron in a substrate.

The present invention does not employ an oxidizing agent and therefore generates a layer of amorphous silicon. Additionally, the present invention has the
20 ability to treat substrates with iron content in addition to those with non-metallic composition (e.g. carbon, silicon).

U.S. Patent 4,671,997 issued on June 9, 1987 to Francis S. Galasso, et al. for "Gas Turbine Composite
25 Parts" utilizes multiple layers of silicon carbide (SiC) and silicon nitride (SiN) on gas turbine engine environments. The protective coatings are deposited at high temperature with organochlorosilanes as the reactive precursor.

30 U.S. Patent 4,714,632 issued on December 22, 1987 to Alejandro L. Cabrera discloses a "Method of Producing

5 Silicon Diffusion Coatings on Metal Articles" where a
silicon diffusion coating is formed on metal objects by
first preheating in a reducing atmosphere.

U.S. Patent 4,173,661 issued on November 6, 1979 to
Bernard Bourdon for a "Method for Depositing Thin Layers
10 of Materials by Decomposing a Gas to Yield a Plasma"
discloses a method for depositing thin layers of
materials in the manufacture of silicon semi-conductor
devices by applying a high-frequency, alternating voltage
between a conductive earth surface and a conductive
15 target surface located on opposite sides of a substrate
to form a plasma in a chamber in the vicinity of the
substrate.

U.S. Patent 5,299,731 issued on April 5, 1994 to A.
Nimal Liyanage et al. for a "Corrosion Resistant Welding
20 of Stainless Steel" discloses a process for welding
stainless steel tubing in the presence of an inert gas
having a silicon base gas in particular SiH_4 . The
stainless steel welding process of the '731 patent
discloses utilization of a silicon containing gas, with
25 argon for a purge.

U.S. Patent 5,480,677 issued on January 2, 1996 to
Yao-En Li et al. for a "Process for Passivating Metal
Surfaces to Enhance the Stability of Gaseous Hydride
Mixtures at Low Concentration in Contact Therewith"
30 discloses the use of temperatures of less than the
passivating agent gaseous hydride decomposition

5 temperature, and uses silane and other gaseous hydrides
in their original form (molecular structure) to adsorb to
a metal surface.

U.S. Patent 6,511,760 issued on January 28, 2003 to
Gary A. Barone et al. discloses a method for passivating
10 the interior surface of a gas storage vessel where
silicon deposition is controlled to apply one or more
layers of silicon to the interior surface of a vessel
under pressure and heat.

15 SUMMARY OF THE INVENTION

The present invention provides a method of
passivating any surface of a substrate to protect a
surface against corrosion, the undesirable effects on a
vacuum environment, or both. The invention provides a
20 novel chemical deposition process through which a
substrate is coated with silicon to impart properties for
application in corrosive and/or vacuum environments. The
use of single to multiple deposition layers with
intermediate changes in process temperature, pressures
25 and time has been found to impart coatings that provide
enhanced properties to the substrate being treated that
include, but are not limited to, application in corrosive
environments for improved resistivity, and application in
vacuum environments to reduce offgassing, outgassing, and
30 hydrogen permeation of substrates. The substrate may
have enhanced properties for vacuum environments, such

5 as, for example, low (10^5 to 3.3×10^3 Pa), medium (3.3×10^3
to 10^{-1} Pa), high (10^{-1} to 10^{-4} Pa), very high (10^{-4} to 10^{-7}
Pa), ultrahigh (10^{-7} to 10^{-10} Pa), and extreme ultrahigh
(less than 10^{-10} Pa).

The substrate surface which may be coated can
10 include an interior surface, as well as, or alternately,
any other substrate surfaces. The present invention also
provides substrates having contact surfaces which have
been passivated in accordance with the method of the
present invention to impart properties for improved
15 resistance to corrosion and reduce the release of gas
molecules subjected to a vacuum environment.

In the method of the present invention, a substrate
is placed in an environment, such as, for example, a
treatment chamber, which may be controlled to carry out
20 the steps of the method. The method may be carried out
using the substrate itself or with the substrate housed
in a treatment chamber. In the method of the present
invention, the surface of a substrate is initially
preconditioned by dehydrating the substrate surface. In
25 the dehydration step, the substrate is heated to a
temperature in a preferred range of from about 20°C to
 600°C for a preferred duration of from about 10 to 240
minutes. The substrate is preferably heated in an inert
gas or in a vacuum.

30 After the surfaces of the substrate have been
dehydrated, the environment surrounding the substrate

5 surface or treatment chamber is evacuated. A silicon
hydride gas is introduced into the environment
surrounding the substrate surface or treatment chamber.
The substrate and gas contained therein are heated and
pressurized to decompose the silicon hydride gas in the
10 treatment chamber. The heating of the silicon hydride
gas may be done prior to, during or after the
introduction of the gas into the treatment chamber.
Preferably, the treatment chamber may be heated and then
followed by the introduction of the silicon hydride gas.
15 As the gas decomposes, a layer of silicon is deposited
on the surface of the substrate.

The duration of the silicon deposition step and the
pressure of the gas is controlled to prevent the
formation of silicon dust in the substrate or treatment
20 chamber. At the end of the silicon deposition step, the
substrate environment or treatment chamber is cooled and
held at a temperature for a period of time, and is purged
with an inert gas to remove the silicon hydride gas. The
purging may take place prior to, after or while the
25 substrate is cooling. Preferably, the purging is done as
the substrate is being cooled. If the silicon layer
completely covers the surface of the substrate, the
substrate is then evacuated and cooled to room
temperature. If the silicon layer does not completely
30 cover the substrate surface, the silicon deposition step
is repeated until the substrate surface is completely

5 covered and thereby passivated.

In the method of the present invention, the silicon hydride gas is preferably selected from the group comprising SiH_4 and $\text{Si}_n\text{H}_{n+2}$. The silicon hydride gas is heated to a temperature approximately equal to the gas's decomposition temperature, preferably to a temperature in the range of from about 300°C to 600°C . Preferably, the silicon hydride gas is pressurized to a pressure in a preferred range of from about 1×10^{-7} torr to 2500 torr, and in a particularly preferred range of from about 100 torr to 250 torr.

The present invention also provides a corrosion resistant substrate or component having a passivated surface. For example, the substrate may comprise metal (ferrous and non-ferrous), glass, carbon, copper, quartz, nickel-containing ferrous alloys, titanium, aluminum and ceramics. The surface of the substrate has an average surface roughness RA. A silicon layer is formed over the substrate surface to passivate the surface. The silicon layer is formed from a plurality of layers of silicon and is substantially free of silicon dust. Preferably from one to ten layers of silicon may be applied.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of the present invention is described below with reference to a substrate. However, it should be appreciated to those of ordinary skill in the art that

5 the method of the present invention may by used to passivate the surface of a component or substrate, and in particular substrates which have undesirable traits when exposed to vacuum conditions or corrosive substances that would benefit from passivation. The method of the
10 present invention may by used to passivate the surfaces of substrates which are comprised of metal (ferrous and non-ferrous), glass, carbon, copper, quartz, nickel-containing ferrous alloys, titanium, aluminum and ceramics. The passivation of a substrate surface which
15 contacts a corrosive substance or molecules, such as, for example, organo-sulfurs, hydrogen sulfide, alcohols, acetates, metal hydrides, hydrochloric acid, nitric acid, or sulfuric acid and aqueous salts, serves to protect the surface against corrosion. The passivation of a substrate
20 surface also provides benefits to the substrate in vacuum environments to reduce undesirable effects, including offgassing and outgassing, and hydrogen permeation of substrates.

In the method of the present invention, the surface
25 to be passivated is initially preconditioned. Successive layers of silicon are then applied to the surface under controlled conditions where the surface is cooled and maintained at a temperature for a period of time between successive deposition layers. Preferably, silicon
30 deposition layers are applied until the silicon layer covers the entire surface area of the substrate. The

5 method may be carried out on or within the substrate
itself, or by placing the substrate in a controlled
environment, such as, for example, a treatment chamber.

The surface of the substrate is initially
preconditioned by removing any water adsorbed on the
10 substrate metal surface. In the dehydration step, the
vessel is heated to a temperature in the preferred range
of from about 20°C to 600°C for a time period of a
preferred duration from about 10 minutes to 240 minutes
(4 hours). During the dehydration step, the treatment
15 chamber containing the substrate to be passivated is
either evacuated or filled with an inert gas (noble gases
or nitrogen). At the end of the dehydration process, the
treatment chamber is evacuated to remove the vaporized
water.

20 After the treatment chamber is dehydrated and
evacuated, silicon hydride gas, such as SiH_4 or Si_2H_6 , is
introduced onto the substrate surface or into the
treatment chamber containing the substrate. Preferably,
the pressure of the silicon hydride gas is at a preferred
25 range between about 1×10^{-7} torr to 2500 torr, and a
particularly preferred range of from about 100 torr to
250 torr. The substrate or component, and gas contained
in the treatment chamber, is heated to a temperature
approximately equal to the gas decomposition temperature
30 if it is not already at that temperature as a result of
the dehydration step. Preferably, the substrate and gas

5 are heated to a temperature in the preferred range of
from about 300°C to 600°C. The silicon hydride gas may
be introduced under heat, or introduced at room
temperature and subsequently heated. At these pressures
and temperatures, the silicon hydride gas decomposes into
10 silicon and hydrogen gas at or near the substrate
surface. The silicon formed during the decomposition
process attaches to the surface of the substrate or
component being treated.

The duration of the silicon deposition process is
15 controlled in accordance with the method of the present
invention. Under the above-described conditions, the
decomposition of silicon hydride gas in the treatment
chamber may eventually also form an undesirable by-
product referred to herein as silicon dust as a result of
20 pressure, time and temperature. Silicon dust is the
result of the silicon hydride gas reacting with itself to
form silicon and hydrogen gas. This gas phase nucleation
forms silicon dust which will settle to the surface of
the substrate or treatment chamber by gravity and may
25 compromise the integrity of the silicon layer being
formed on the substrate surface. The silicon dust may
also create a physical barrier between successive layers
of silicon in the passive layer.

The formation of silicon dust may be affected by the
30 duration of the deposition process, the pressure of the
gas, and the presence of contaminants on the surface of

5 the substrate, or a combination of any or all of them.
In order to facilitate the prevention of the formation of
silicon dust, the duration of the silicon deposition
process must be controlled and limited to a period in a
preferred range of from about 1 minute up to about 480
10 minutes (8 hours). The silicon deposition process may be
abbreviated as one way to prevent the formation of
silicon dust. However, the layer of silicon may not
completely cover the entire substrate surface after one
silicon deposition cycle. Therefore, the silicon
15 deposition cycle may be repeated several times to build
up the passive layer of silicon to the requisite
thickness. However, the performance of the substrate may
benefit from a single deposition layer. Preferably,
performance of the substrate may be optimized by the
20 deposition of one to ten layers of silicon on the
substrate surface, independent of the surface roughness.
It may be particularly preferred to optimize performance
by having six silicon layers deposited on the substrate
surface.

25 After the first silicon deposition cycle, the
treatment chamber containing the substrate is purged with
an inert gas to remove the silicon hydride gas. If the
layer of silicon does not completely cover the surface of
the substrate, the silicon deposition cycle may be
30 repeated. Prior to deposition of a subsequent silicon
layer, the substrate surface is cooled and permitted to

5 remain at a lower temperature to optimize the surface
properties in preparation for subsequent silicon layer
deposition. Preferably, the substrate surface is cooled
to a range of about 50°C to 400°C, and permitted to
remain at the cooled temperature for about 5 to 100
10 minutes.

That is, a rough or smooth (electropolished or
polished) surface with an RA less than about 20
microinches may derive the benefits of the method with a
single deposition cycle. The number of layers for vacuum
15 atmosphere performance of a substrate may be optimized
independent of surface roughness. The number of layers
for improved resistance to corrosion may be optimized
independent of surface roughness.

After the passive layer of silicon is formed, the
20 treatment chamber containing the substrate is cooled to a
preferred range of about 50-400°C, held for a preferred
time duration of from about 5 to 100 minutes, and is
purged with an inert gas to remove the reactive silicon
hydride gas. This inert gas purge ensures that the
25 decomposition reaction of the silicon hydride is stopped
to reduce unwanted gas phase nucleation problems which
occur due to reaction of the silicon hydride components
with themselves as opposed to the surface of the
substrate or the treatment chamber. After the final
30 purging step, the treatment chamber containing the
substrate is evacuated and cooled to room temperature.

5 The passive silicon layer deposited on the substrate surface may be about 100 to 50,000 angstroms thick.

 The method has use in passivating substrates which may be exposed to a corrosive substance or used in a vacuum environment, or both, to impart beneficial
10 properties to the substrate. The method of the present invention has particular use for passivating substrates which may be used in environments which contain or may subject the substrate to a corrosive element or substance. The method of the present invention may be
15 used to impart resistive properties to a substrate to minimize undesirable effects of a corrosive substance such as for example chemisorption of other molecules; reversible and irreversible physisorption of other molecules, and catalytic activity with other molecules;
20 allowing of attack from foreign species, resulting in a molecular, structural and/or cosmetic breakdown of the substrate surfaces and/or bulk; or any of the aforementioned combinations. In addition, the method of the present invention has particular use for passivating
25 substrates which may be used in vacuum environments. The method of the present invention may be used to impart chemically resistive properties to a substrate to minimize undesirable surface effects in a vacuum environment on a substrate such as for example offgassing
30 or outgassing of volatile materials (e.g. water vapor and organics) from a substrate under vacuum environments

5 resulting in extensive time required to reach a target
vacuum and/or the inability to achieve a target vacuum
and/or the inability to maintain a target vacuum;
hydrogen permeation of a substrate under vacuum
environments through coating on the inside and/or outside
10 whereas the inner portion is subjected to vacuum; or any
of the aforementioned combinations.

Within performance in a vacuum atmosphere, the
deposition on the substrate may improve the substrate
performance with respect to deleterious effects of
15 hydrogen permeation.

The invention is useful for imparting improved
properties on the surface of a substrate. Substrates to
which the method may be applied may have one or more
surfaces. The invention may be used to coat one or more
20 surfaces of a substrate. For example, a substrate may
have an interior surface and an exterior or outside
surface. The method may also impart improved resistance
to, or prevention of, hydrogen permeation by application
of a coating on the inside of a substrate which is
25 subjected to a vacuum. The method may also impart
improved resistance to, or prevention of, hydrogen
permeation by application of a coating on the outside of
a substrate where the inside of the substrate is
subjected to a vacuum. Alternately, the coating may be
30 provided on an inner surface and an outer surface of a
substrate.

5 Although the method may be carried out using a
treatment chamber to house the substrate during the
process steps, it will be understood that the substrate
itself, depending on its configuration, may serve as its
own treatment chamber where the method may be carried out
10 within the substrate.